

SCIENCE FOR GLASS AND CERAMIC PRODUCTION

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OPACIFIED GLAZES BASED ON LIQUATING GLASS OF LOW-ALKALI COMPOSITIONS

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The vitrification processes in the $\text{Na}_2\text{O} - \text{MgO} - \text{CaO} - \text{B}_2\text{O}_3 - \text{SiO}_2$ system and the effect of the heat-treatment conditions on the location of the liquation regions, the nature, the structure, and the phase composition of liquating glasses and on the kinetics of the liquation processes are studied. Physicochemical parameters of the glasses that corroborate the presence of liquation-phase inversion are identified. Compositions for liquating glazes with a minimum content of zirconium-bearing opacifying components are developed.

Liquation is the most effective method for producing opacified coatings with a controllable degree of opacification. The advantages of coatings opacified by liquation include the absence or a minimum content of scarce opacifying agents and, as a rule, few-component formulas, high thermal resistance of the coating, the absence of scarce or toxic components in it, and the possibility of controlling the degree of opacification. However, few practical compositions for opacified glazes produced by liquation are known. Considering the advantages of liquating coatings, it is expedient to develop new glaze compositions and study their structure and properties.

An analysis of the literature shows that sufficient attention has been given to the general theory of the evolution of the liquation process. At the same time, practical aspects related to liquid-phase separation in glaze glasses and coatings call for further investigation.

The system selected for investigation was the $\text{Na}_2\text{O} - \text{MgO} - \text{CaO} - \text{B}_2\text{O}_3 - \text{SiO}_2$ system in the region of low-alkali compositions, due to its strong tendency for liquation phase separation and crystallization.

The experimental compositions of the investigated glasses involved a number of cross sections of the indicated system, and the oxide content was varied in a wide range (here and elsewhere molar content is indicated, %): 5–10 Na_2O , 2.5–5 MgO , 5–50 CaO , 5–30 B_2O_3 , 35–70 SiO_2 .

The experimental data indicate that with a temperature of synthesis equal to 1400–1450°C the great majority of the glasses studied became well melted and clarified. Only high-silicon (67.5–70.0 SiO_2) and high-calcium (45–50

CaO) glasses contained unmelted inclusions. There are extensive regions of opalescent and opacified glass in the considered cross sections of the system. The presence of such regions can be related to liquation phenomena, since these compositions are positioned near liquation fields on the diagrams of the particular systems.

The electron microscope photographs clearly exhibit a liquation structure in both the opalescent and opacified glasses. The liquation character of the opacification is confirmed by the data of an x-phase analysis: all the glasses considered are x-ray-amorphous. The liquation is dropwise and, less frequently, two-skeleton. The number of drops per unit volume and the drop size vary with the glass composition. As the Na_2O and B_2O_3 content increases, the drop size decreases and the number of drops per unit volume decreases sharply. Here the degree of glass opacification is reduced all the way down to clarification.

An increase in the CaO content also leads to a decrease in the mean size of the drops and an increase in their number per unit volume; however this is less substantial than in the case of Na_2O and B_2O_3 . Here, passage from the two-skeleton liquation structure to the drop structure takes place.

As regards MgO , an increase in its content from 2.5 to 5.0% fosters substantial development of liquation separation.

The phase composition of the liquating glasses was determined by means of local x-ray spectral analysis of the element composition, employing an electron microprobe as part of a Camebax x-ray microanalyzer (made by Cameca) provided with a PC-based automation system.

The analysis revealed an inversion of the liquation phases in going from high-silicon to low-silicon glasses with

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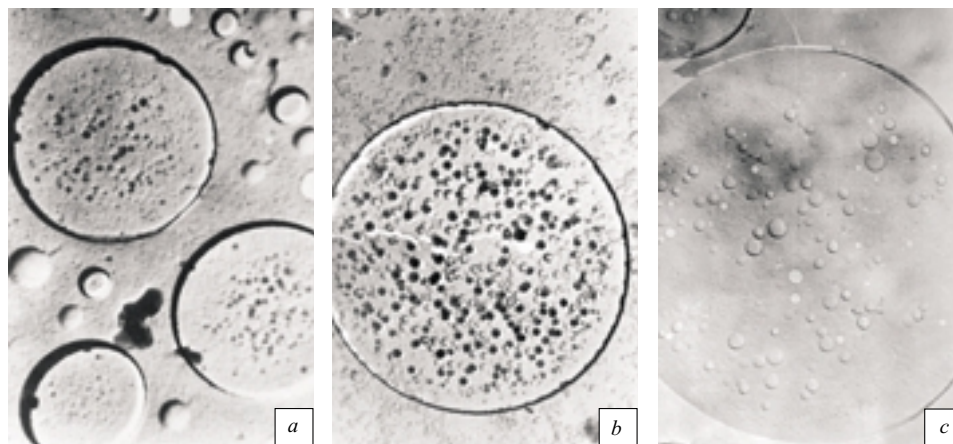


Fig. 1. Electron microscope photographs of glass of composition $7.5\text{Na}_2\text{O} \cdot 2.5\text{MgO} \cdot 15\text{CaO} \cdot 20\text{B}_2\text{O}_3 \cdot 55\text{SiO}_2$ treated at 800°C for 2 h (a), 4 h (b), and 6 h (c).

an increased content of modifier oxides. In the first case, the glass matrix is enriched in SiO_2 , while CaO , Na_2O and, evidently, B_2O_3 are concentrated in the drops. In glasses containing over 20% CaO , the matrix is formed of a phase enriched in B_2O_3 , CaO , Na_2O , and MgO , whereas SiO_2 is concentrated primarily in the drop phase.

The majority of glaze coatings are vitreous materials whose final structure is formed in the course of fusion, and therefore, the study of structural modifications in glasses under heat treatment is of substantial scientific and practical interest.

The effect of heat treatment on the structure of liquating glasses was studied in two ways: forced crystallization in a gradient furnace within the temperature interval $650 - 1000^\circ\text{C}$ for 1 h, and a hold of samples in the furnace at a selected temperature. It is found that as a result of heat treatment, the boundaries of the regions of opacified and opalescent glass expand. All opacified glasses containing less than 30% CaO and 65% SiO_2 are x-ray amorphous. After heat treatment above 900°C , the appearance of a crystalline phase, namely, wollastonite, is observed in glasses bearing over 30% CaO . Heat treatment at 700°C expands the boundaries of metastable immiscibility in glasses of all cross sections of the system, and heat treatment at 800 and 900°C has virtually no effect on the expansion of the bounds of liquation.

According to the electron microscope data, slightly opalescent and clear glasses have a microheterogeneous structure with a heterogeneity size below $0.1 \mu\text{m}$. Heat treatment for 2 h at 700°C leads to the appearance of a drop structure with a drop size of $1.5 - 2.1 \mu\text{m}$, and heat treatment at 800°C for 2 h leads to an even greater increase in the size of the drop-type liquation heterogeneities. The type of phase separation is largely determined by the previous thermal history of the sample. The same sample forms a drop structure after a hold at higher temperatures and after a hold at lower temperatures forms a two-skeleton structure.

As a result of studying the effect of the heat-treatment procedure on the liquating-glass structure, it was found that phenomena of secondary phase separation actively develop in the $\text{Na}_2\text{O} - \text{MgO} - \text{CaO} - \text{B}_2\text{O}_3 - \text{SiO}_2$ system (Fig. 1).

A special feature of phase separation in the glasses considered is the following. The size of the larger heterogeneous regions formed as a result of the primary separation grows with increasing duration of heating at a temperature of 800°C , while the size of the small drops change to a lesser extent. The first phenomenon is typical of the primary separation; the secondary separation, if it takes place in a phase whose composition reaches the bimodal-liquation boundary, should not depend on the glass heating duration.

Additional heating of samples at a lower temperature fosters an increase in the size of the secondary drops without having a perceptible effect on the primary-drop size. Figure 2 shows the structure of glasses subjected to a two-stage heat treatment.

It is known [1, 2] that a phase rich in alkali undergoes a secondary phase separation more readily, since upon increase in temperature, such a phase undergoes more significant composition modifications. This suggests that the drop phase contains mostly an alkali metal oxide, which was corroborated by an x-ray spectral microprobe analysis. It should be noted that a multistage heat-treatment procedure involving a 2-h hold at 900°C and then a hold for the same time at 700°C results in the appearance of a third-order separation within the secondarily separated phase (see Fig. 2).

The liquation kinetics was studied by quantitative processing of electron microscope photographs of glass structures at different stages of phase separation. The studies were carried out at a temperature of $700 - 800^\circ\text{C}$ with varying heat-treatment duration. The kinetic parameters of phase separation (the rate of nucleation of phase heterogeneity regions and their growth rate) were determined by calculating the following quantitative parameters of the liquation structure: the mean radius of the particles R ; the total number of

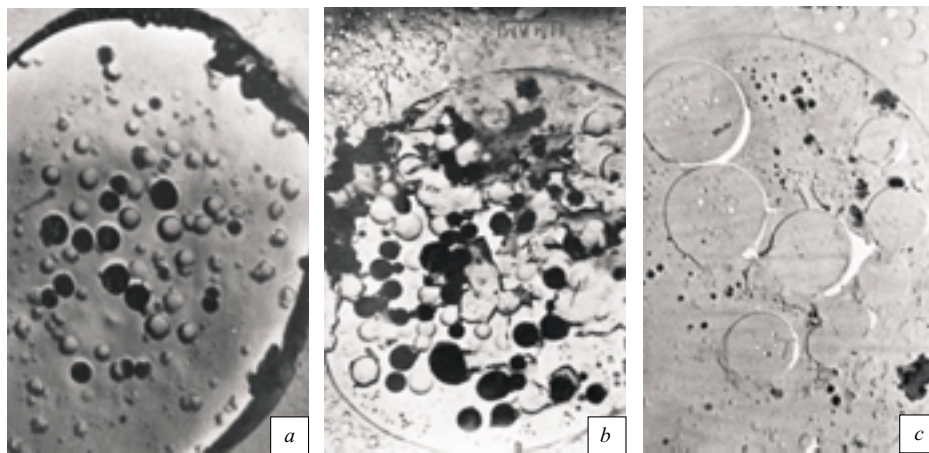


Fig. 2. Electron microscope photographs of glass of compositions $5\text{Na}_2\text{O} - 2.5\text{MgO} - x\text{CaO} - 20\text{B}_2\text{O}_3 - (72.5 - x)\text{SiO}_2$ heat-treated at 900°C for 2 h and at 700°C for 2 h, with a CaO content of 5% (a), 10% (b), and 20% (c).

particles per unit volume N ; the function of size distribution of the particles $f(R_i)$; the ratio of the coexisting-phase volumes V/V_0 . All the parameters were determined in accordance with the method of [3] by statistical processing of electron microscope photographs that register different stages of the phase separation.

The time dependence of the coexisting-phase volumes is used most frequently to determine attainment of the equilibrium state in studying phase separation processes. It is found that a volume of the drop phase close to the equilibrium value is reached after 4-h treatment of the glass.

The value of N in the glasses decreases with increasing heat-treatment temperature. The growth rate of the mean radius of the droplike heterogeneities reaches a maximum value at temperatures close to 700°C . As the heat-treatment temperature increases, the volume of the drop phase decreases intensely. Figure 3 presents the change in the size distribution function of the drop phase in relation to the heat-treatment duration. The curves obtained point to both one-modal and bimodal distribution functions, which is apparently related to the simultaneous occurrence of the processes of nucleation, dissolution, and growth of the micro-heterogeneity regions [4].

DTA studies of the glasses revealed the presence of two endothermic effects typical of liquating glasses. The recording of the vitrification temperatures indicates the existence of two vitreous phases. The softening temperature of the lower-melting phase corresponds to $625 - 670^\circ\text{C}$, and that of the other phase corresponds to $720 - 800^\circ\text{C}$.

Physicochemical properties of glasses of the system considered are shown in Fig. 4. The results obtained are interpreted taking into account the two-phase liquation of the glasses. The presence of inflections on the curves of the dependences is due to inversion of liquation phases. Thus, with a CaO content of 15–20%, the matrix is formed by a siliceous phase that in this case determines the physico-

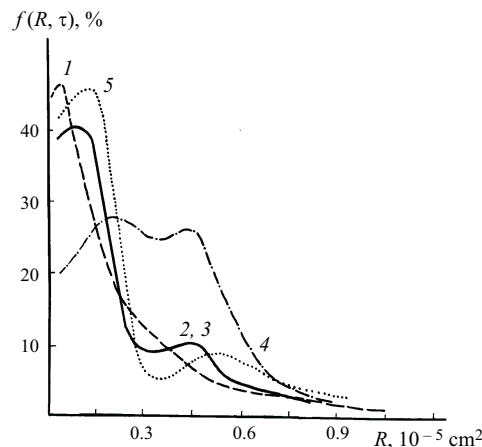


Fig. 3. Change in the size distribution function of the drop phase in relation to the duration of heat treatment of the glass at 700°C : 1, 2, 3, 4, and 5) 1, 3, 6, 12, and 24 h, respectively.

chemical properties of the glass. Since this phase has lower TCLE values, a higher softening temperature and microhardness, and a somewhat lower water resistance due to the presence of three-coordination boron, glasses in which this phase serves as the matrix phase possess the corresponding properties. In glasses containing over 20% CaO, the matrix is formed by a phase enriched in B_2O_3 , CaO, and Na_2O . Accordingly, the properties of these glasses are determined by the characteristics of the boron–calcium–sodium matrix: the TCLE exceeds the calculated value, due to the relatively large amount of Na_2O in this phase; the microhardness and the softening temperature are slightly lower than in glasses with a high-silicon matrix; the chemical resistance to water is rather high.

The studies of the physicochemical properties of the glasses indirectly support the results obtained in studying the corresponding glasses by the electron paramagnetic reso-

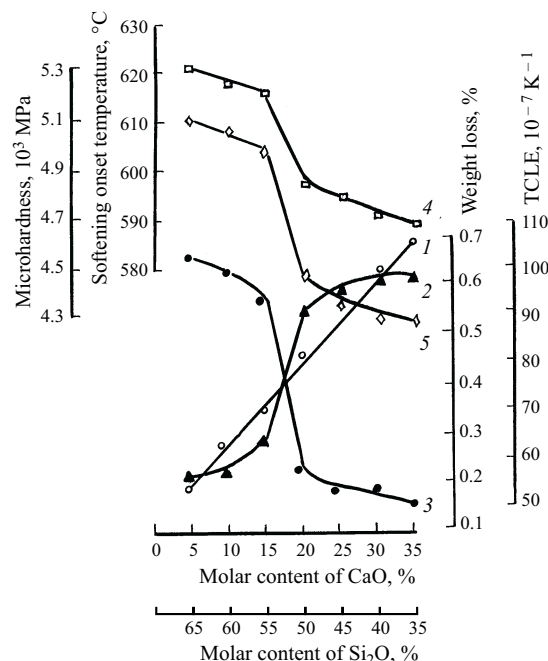


Fig. 4. Dependence of the physicochemical properties of glasses of the Na₂O–MgO–CaO–B₂O₃–SiO₂ system on the CaO and SiO₂ content: 1 and 2) calculated and experimental values of the TCLE; 3) microhardness; 4) initial softening temperature; 5) weight loss of the glass in H₂O.

nance method, namely, three-coordination boron exists mainly in the high-silicon phase, and four-coordination boron in the phase enriched in boron.

A spectroscopic study of the structure of the calcium-bearing boron-silicate glasses established the presence of the following structural groups: [SiO₄], [BO₃], and [BO₄]. Calcium oxide has a significant effect on the degree of polymerization of the anion skeleton. As the CaO content in the glass decreases from 25 to 5%, the degree of polymerization of the main structural groups increases, which provides for conversion from chain and laminar patterns of the structural groups to skeleton patterns. Calcium oxide behaves like a modifier cation that facilitates rupture of Si–O–Si bonds. In the glasses of the system considered, calcium oxide also affects the coordination conversion of [BO₃] to [BO₄]. CaO retains but weakly its oxygen ion and thus meets the coordination requirements of boron. A structural feature was identified in calcium-boron-silicate glasses that is caused by incomplete conversion of [BO₃] groups to [BO₄] groups in glasses in which the total amount of metal oxides is sufficient for complete conversion of boron to four coordination.

For a more detailed study of the glass structure, IR spectra of heat-treated glasses were recorded. An analysis of IR spectra of initial and heat-treated glasses within the temperature range of 600–950°C with a 50°C step and a 2-h hold makes it possible to conclude that with increasing heat-treatment temperature, insignificant growth of the intensity of the absorption bands in the region of 1250–1500 and 680–

700 cm⁻¹ with maxima at 1400 and 700 cm⁻¹, respectively, occurs. The first band is caused by vibrations of three-coordination boron in complexes with polymerized [BO₃] groups, and the second band also relates to three-coordination boron and reflects extraplanar deformation vibrations in [BO₃] groups. An increase in the heat-treatment temperature from 600 to 950°C results in an increased amount of three-coordinated boron, which agrees well with electron microscope data that indicate that liquation separation is intensified here.

Glaze glasses containing 5 wt.% VGO-2 clay as a milling additive were fused on ceramic crock in the temperature interval of 700–1050°C with a 1-h hold at the maximum temperature. Formation of lustrous, dull, and semidull coatings with varying degrees of opacification was observed in all cross sections of the system. Lustrous opacified coatings are formed in the region bounded by the following component content (%): 7.5–10.0 Na₂O, 2.5–5.0 MgO, 10.0–20.0 CaO, 20.0–25.0 B₂O₃, 42.5–65.0 SiO₂. Compositions with an increased CaO content produce dull coatings of various textures ranging from velvety to stony.

Electron microscope studies of lustrous coatings and coatings with a silky dull surface indicated that opacification is caused exclusively by liquation processes. Lustrous glazes have a liquation structure of the drop type (with a drop size of 0.2–0.4 μm) and the two-skeleton type. As the CaO content is increased to 20% and the B₂O₃ content is increased somewhat, the liquation type is sharply modified: two-skeleton liquation prevails, individual sites of merged heterogeneities of closed labyrinth shape are formed, inside which small-sized secondary liquation drops (up to 0.1 μm) are found.

In studies of coatings produced under industrial conditions, it was found that liquation glazes are very sensitive to the temperature conditions of the firing, and temperature differences above 20°C cause significant variations in the degree of opacification. These fluctuations are within the limits of 5–7% with a total whiteness index of 65–72%, which causes certain difficulties related to the difference in the color tone of the coating.

Here the coatings have a narrow firing temperature interval, namely, 900–940°C. To improve the spreading and opacification of the coatings, the optimum-range compositions were modified by partial replacement of Na₂O by K₂O and introduction of an opacifying modifier. The modifier was ZrO₂ in an amount of 1–3% (over 100%); K₂O was introduced instead of Na₂O in an amount of 2–3%. This made it possible to stabilize the opacification of the glaze coating. The optimum additives were 3% ZrO₂ and 2% K₂O. In fusing glaze coatings of the modified compositions, it was observed that their texture is modified with increase in the firing temperature. Heat treatment at a temperature of 800–850°C with a 0.5 h hold provides good opacification, smooth spreading, and absence of defects.

Studies of the glaze structure using electron microscopy indicated that deep and middle layers of the coating have a two-skeleton liquation structure, inside which finer drops are located. On the surface of the fire mirror liquation is absent, and only single crystals are observed that presumably belong to zircon and cannot be identified by the x-ray phase analysis method due to their small sizes.

As a result of the investigations, liquating glaze coatings were synthesized.

Physicochemical parameters of opacified liquating glazes of optimum compositions

Firing temperature interval, °C	920 – 960
TCLE, 10^{-7} K^{-1}	48.7 – 54.3
Heat resistance, °C	170 – 190
Cold resistance, cycles	50
Water resistance (weight loss), %	0.02 – 0.03
Contact angle of wetting at 950°C, deg	50 – 60
Whiteness, %	72 – 76
Luster, %	62 – 65
Microhardness, MPa	6520 – 6770

The opacification of the glazes is provided by the capacity of the bivalent cations for causing separation of the glass into droplike and continuous phases that have different refraction indices. Stabilization of the properties of the coating is accomplished by introduction of small opacifier additives. The glaze is characterized by a high wetting capacity, which

can be attributed to the “lubricating” effect of the matrix phase of the liquation structure of the coating, which is a special feature of liquating glazes [5]. Based on the temperature dependence of the contact angle of wetting in the optimum glaze composition, it was established that the contact angle of wetting lies within the interval of 50 – 70° in the optimum-temperature region. The glaze viscosity is $(2.1 - 2.7) \times 10^3 \text{ Pa} \cdot \text{sec}$, which somewhat exceeds the viscosity of opacified glazes of known compositions. This is caused by a liquation structure with a minimum content of the crystalline phase.

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